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(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors: KOLTHAMMER, Brian ; 54 Royal Oak Circle, Lake Jackson, TX 77566 (US). TRACY, John, C. ; 107 Old Angleton Road, Lake Jackson, TX 77566 (US). CARDWELL, Robert, S. ; 106 Any Way, Lake Jackson, TX 77566 (US). ROSEN, Robert, K. ; 1800 Rivercrest Drive, Apartment 210, Sugar Land, TX 77478 (US).

(74) Agent: WHITE, L., Wayne; The Dow Chemical Company, Patent Department, B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US).

(54) Title: SUPPORTED HOMOGENEOUS CATALYST COMPLEXES FOR OLEFIN POLYMERIZATION

(57) Abstract

A supported catalyst complex having a Group 4 metal cyclopentadienyl derivative and an aluminoxane reacted with silica which show improved resistance to catalyst poisoning. The supported catalyst composition is particularly suitable for producing homogeneous ethylene polymers and copolymers having a narrow molecular weight distribution. The invention further includes the process of preparing the supported catalyst compositions and their use as olefin polymerization catalysts. The catalyst support is prepared by contacting silica with an aluminoxane, preferably either methylaluminoxane or modified methylaluminoxane.

techniques. The MWD can also be approximated by the I_{10}/I_2 ratio, as described

in ASTM D-1238. The I_{10}/I_2 ratio is also an indicator of the shear sensitivity and

processibility for ethylene polymers. Low density polyethylenes (LDPE) typically

have a higher I_{10}/I_2 ratio than linear low density polyethylenes (LLDPE) or ultra

5   low density polyethylenes (ULDPE) and are easier to melt process in fabrication

equipment.

Recently, ethylene polymers having a narrow MWD were introduced.

These polymers were produced using a so-called "single site catalyst."

10

In EP 0 416 815, published March 13th, 1991, there are disclosed certain

constrained geometry complexes comprising a strain-inducing delocalized pi-

bonded moiety and metals of Groups 4 to 10 of the Periodic Table of the Elements.

Such compositions formed catalysts in the presence of activating cocatalysts such

15   as methylaluminoxane, aluminum alkyls, aluminum halides, aluminum

alkylhalides, Lewis acids, ammonium salts, non-interfering oxidizing agents, and

mixtures of the foregoing.

In U.S. Patent Nos. 5,026,798 and 5,055,438, certain Group 4

20   metallocene compounds having a heteroatom ligand were also used in combination

with aluminoxanes as olefin polymerization catalysts.

In EP 0 418 044, published March 29th, 1991), certain cationic derivatives

of the foregoing constrained geometry catalysts are disclosed as olefin

25   polymerization catalysts. These cationic catalysts have excellent catalytic activity

but unfortunately they are undesirably sensitive to polar impurities contained in the

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olefin monomers, the polymerization mixture, or even the polymerization reactor

which act as catalyst poisons. When the polar impurities are present, the catalyst

lifetimes have been limited and the molecular weights of the resulting polymers

have been reduced. Thus, special handling is required to eliminate such polar

5   impurities.

Trialkylboron, trialkylaluminum and aluminoxane compounds have been

employed to remove catalyst poisons from biscyclopentadienyl-containing olefin

polymerization catalysts. Such adjuvants have proven to be ineffective in

10   combating the inhibition or poisoning of the cationic catalysts and they may actually

interfere with the desired catalytic polymerization process. For example, in J. Am.

Chem. Soc. 113, 8570-8571 (1991), it has been reported that the use of

aluminoxanes in combination with biscyclopentadienyl-containing cationic olefin

polymerization catalysts results in the detrimental interference with the catalyst for

15   propylene polymerizations. Catalyst poisoning is a problem, particularly for

cationic catalysts.

Accordingly, there is a need for new or improved organometallic catalyst

compositions, particularly supported homogeneous catalyst compositions, that (1)

20   are resistant to the effects of polar impurities and other catalyst poisons, and that (2)

have extended catalyst lifetimes and improved polymerization efficiencies.

Additionally, there is a need for new or improved organometallic catalyst

compositions, particularly homogeneous catalyst compositions, which can be used

25   in either gas-phase olefin polymerization reactions, slurry olefin polymerization

reactions or solution olefin polymerization reactions. The cationic catalysts are

known to be quite useful in solution polymerizations but are generally considered less useful in slurry polymerizations, and of even less value in gas-phase polymerizations.

5　　　　　Various techniques have been tried to overcome the low polymerization activities of the catalysts. For example, alkylaluminoxane cocatalysts were included in molar ratios of greater than 500:1 relative to the organometallic catalyst species (Chien, et al., J. Pol. Sci., Part A, 26, 2639,(1987)). Others have tried drastic polymerization conditions (e.g., very high reaction pressures) to improve

10　　　polymerization rates and efficiencies. Such efforts are illustrated in EP 0 260 999. In WO 91/09882, published July 11th, 1991, it has been reported that metallocene-alumoxane catalysts produce polymers of generally lower molecular weight and comonomer incorporation than desired. The application further reports that it would be desirable to support cationic complexes without the

15　　　use of an alumoxane or alkyl aluminum cocatalyst.

Accordingly, there is also a need for an olefin polymerization catalyst that can be used to more efficiently and effectively copolymerize ethylene with higher alpha-olefins, e.g. alpha-olefins having 3 to 18 carbon atoms. In practice, the

20　　　commercial copolymers are made using alpha-olefin monomers having 3 to 8 carbon atoms (i.e., propylene, butene-1, hexene-1, octene-1 and 4-methyl-1-pentene) because of the low rate of reactivity and incorporation of the alpha olefins with larger carbon chains because the traditional Ziegler catalysts are not efficient or effective in incorporating the longer chain comonomers into the polymer. There is

25　　　a need for an olefin polymerization catalyst which is able to efficiently incorporate a large degree of longer chain olefins into a copolymer chain and give a polymeric

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product which has a narrow molecular weight distribution and is homogeneous with respect to branching. The properties and advantages of homogeneous copolymers are described in US Patent 3,645,992.

5   Patents and publications which reflect the technology of vinyl addition polymerization, particularly with respect to olefin polymerization, include U.S. Patent Nos.: 4,808,561; 4,935,397; 4,937,301; 4,522,982; 5,026,798; 5,057,475; 5,055,438; 5,064,8025,096,867; European Patent Publication Nos.: 0 129 368, published December 27th, 1984; 0 260 999 published March 23rd, 1988; 0 277

10   004, published August 3rd, 1988; 0 416 815 published March 13th, 1991; 0 420 431 published April 3rd, 1991; and International Patent publication Nos.: WO 91/04257, published April 4th, 1991; WO 91/14713, published October 3rd, 1991; and WO 92/00333, published January 9th, 1992.

15   The present invention provides new and advantageous supported catalyst compositions, new and advantageous supports for catalyst compositions, a process for preparing these new supports, a process for preparing the supported catalyst compositions, and a process for polymerizing olefins using these new supported catalyst compositions. The new and advantageous supports are prepared by

20   contacting silica with an aluminoxane, preferably either methylaluminoxane or modified methylaluminoxane. The new and advantageous supported catalyst compositions combine these supports with a variety of organometallic catalyst compositions including, for example, constrained geometry catalyst complexes and metallocene catalysts. Olefins may be advantageously polymerized using these new

25   supported homogeneous catalyst compositions, especially ethylene homopolymers and copolymers. Long chain olefins may also be advantageously copolymerized

with short chain olefins using these new supported homogeneous catalyst compositions. Additionally, the new supported homogeneous catalyst compositions are useful in solution polymerization, slurry polymerization and gas-phase polymerization of olefins.
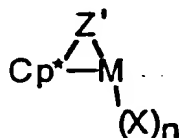
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SUMMARY OF THE INVENTION

The supported homogeneous organometallic catalyst complexes of the present invention are a three-component catalyst system comprising:

10

(a) an organometallic complex of the formula:

$$Cp^* \overset{\overset{\displaystyle Z'}{\diagup\diagdown}}{-} \overset{\displaystyle M}{\underset{\displaystyle (X)_n}{\diagdown}}$$

15   wherein:

M is a metal of Group 4 of the Periodic Table of the Elements,

Cp* is a cyclopentadienyl group bound in an ^{5} bonding mode to M or such a cyclopentadienyl group substituted with from one to four substituents selected from the group consisting of hydrocarbyl, silyl, germyl, halo, hydrocarbyloxy, amine, and mixtures thereof, said substituent having up to 20 nonhydrogen atoms, or optionally, two substituents together cause Cp* to have a fused ring structure;

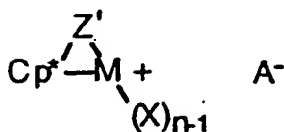Z' is a divalent moiety other than a cyclopentadienyl group or substituted cyclopentadienyl groups, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z' together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 50 non-hydrogen atoms and X is not a cyclopentadienyl or substituted cyclopentadienyl group; and

n is 1 or 2 depending on the valence of M;

(b) a compound or complex capable of converting the organometallic complex (a) into a cationic complex of the formula:

$$Cp^*—\overset{\displaystyle Z'}{\underset{(X)_{n\text{-}1}}{M}} + \qquad A^-$$

5

wherein:

Cp*, Z', M, X, and n are as defined with respect to previous formula I, and

10   A^- is a monovalent, noncoordinating, compatible anion.

(c) a catalyst support in contact with (a) and (b), said catalyst support comprising silica reacted with a methylaluminoxane, a modified methylaluminoxane, or a mixture thereof.

15

The supported organometallic catalyst compositions of the present invention: (a) are resistant to the effects of catalyst poisons, (b) they have extended catalyst lifetimes and improved polymerization efficiencies, particularly with respect to polymerization of long chain olefin monomers, (c) they

20 can be used to provide copolymers, particularly polyolefin copolymers, terpolymers, etc., that have a narrow molecular weight distribution, (d) they provide efficient incorporation of long chain monomers, particularly higher alpha-olefin monomers, into olefinic polymers such that the distribution of long chain monomers in the resultant polymer is homogeneous with respect to both the

25 molecular weight distribution and the distribution of the long chain monomers in the polymer chain, and (e) the novel supported organometallic catalyst

compositions are not restricted to any particular polymerization process, but can be

used in gas-phase polymerization, slurry polymerization or solution polymerization

of olefins.

5   DEFINITIONS

        All reference to the Periodic Table of the Elements herein shall refer to the

Periodic Table of the Elements, published and copyrighted by CRC Press, Inc.,

10   1989. Also, any reference to a Group or Groups shall be to the Group or Groups

as reflected in this Periodic Table of the Elements using the IUPAC system for

numbering Groups.

        Group or Groups - Any references to a Group or Groups shall be to the Group or

15   Groups using the IUPAC system for numbering groups of elements.

        MAO - all references refer to methylaluminoxane.

        MMAO - all references refer to modified methylaluminoxane.

20   Non-coordinating anion - all references refer to an anion that does not complex or

        coordinate with the organometallic complex of component (a), described below, or

        which is only weakly coordinated therewith, thus remaining sufficiently labile to be

        displaced by a neutral Lewis base. A non-coordinating, compatible anion

        specifically refers to a compatible anion which when functioning as a charge

25   balancing anion in the catalyst composition of the invention, does not transfer an

        anionic substituent or fragment thereof to a cationic species of component (a)

        thereby forming a neutral four coordinate metallocene and a neutral metal by-
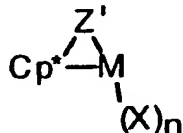
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product.

Homogeneous catalyst complex - all references refer to a catalyst which provides a polymerization product that has a narrow molecular weight distribution and, for copolymers, a random distribution of comonomer molecules along the polymer backbone and are homogeneous between molecules with respect to their comonomer content.

Ziegler catalyst - all references refer to complex generally derived from titanium halide and a metal hydride or a metal alkyl. These complexes and methods for preparation are disclosed in U.S. Patents 4,302,565, 4,302,566, 4,303,771, 4,395,359, 4,405,495, 4,481,301 and 4, 562,169. These catalysts usually operate at atmospheric pressure and may be used to polymerize ethylene to linear polyethylene.

DETAILED DESCRIPTION OF THE INVENTION

The supported organometallic catalyst complexes of the invention are adapted to produce a homogeneous polymer or copolymer. The complexes generally comprise the reaction product of:

(a)   an organometallic complex of the formula:

$$Cp^* - M \overset{\displaystyle Z'}{\underset{\displaystyle (X)_n}{\diagup}}$$

wherein:

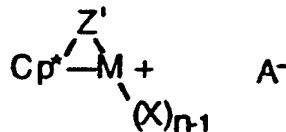M is a metal of Group 4 of the Periodic Table of the Elements,

Cp* is a cyclopentadienyl group bound in an ^{5} bonding mode to M or such a cyclopentadienyl group substituted with from one to four substituents selected from the group consisting of hydrocarbyl, silyl, germyl, halo, hydrocarbyloxy, amine, and mixtures thereof, said substituent having up to 20 nonhydrogen atoms, or optionally, two substituents together cause Cp* to have a fused ring structure;

Z' is a divalent moiety other than a cyclopentadienyl group or substituted cyclopentadienyl groups, said Z' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z' together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 50 non-hydrogen atoms and X is not a cyclopentadienyl or substituted cyclopentadienyl group; and

n is 1 or 2 depending on the valence of M;

(b) a compound or complex capable of converting the organometallic complex (a) into a cationic complex of the formula:

$$\begin{array}{c} Z' \\ Cp^*{-}M^+ \\ (X)_{n\text{-}1} \end{array} \quad A^-$$

wherein:

Cp*, Z', M, X, and n are as defined with respect to previous formula I, and

A$^-$ is a monovalent, noncoordinating, compatible anion.

(c) a catalyst support in contact with (a) and (b), said catalyst support comprising silica reacted with a methylaluminoxane, a modified methylaluminoxane, or a mixture thereof.

defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl ring. The angle, , formed at the metal center between the centroid of the cyclopentadienyl ring and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray

5   diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, , is less than in a similar, comparative complex differing only in the fact that the constrain-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. The

10   angle, ', which is the angle formed between the centroid of the substituted cyclopentadienyl group, M and the substituent attached to M and the cyclopentadienyl group is less than in a comparative complex wherein the substituent is hydrogen and lacks a bond to the cyclopentadienyl group. Preferably, monocyclopentadienyl metal coordination complexes used according to

15   the present invention have constrained geometry such that the smallest angle, , is less than 115°, more preferably less than 110°, most preferably less than 105°. Highly preferably, the average value of all bond angles, , is also less than in the comparative complex.

20   Examples of delocalized -bonded moieties include Cp* as defined hereinafter, as well as delocalized allyl or diene groups. Examples of constrain inducing moieties include - Z'- or -Z-Y- as defined hereinafter, as well as difunctional hydrocarbyl or silyl groups, mixtures thereof, and mixtures of the foregoing with a neutral two electron donor ligand selected from the group

25   consisting of OR^*, SR^*, NR^*_2, or PR^*_2, wherein R^* is as defined hereinafter. Preferred metals are the Group 4 metals with titanium being most preferred.

It should be noted that when the constrain- inducing moiety comprises a neutral two electron donor ligand, the bond between it and M is a coordinate-

30   covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer. A neutral Lewis base, such as an ether or amine compound, may also be associated with the complex, if desired, however, such is generally not preferred.

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More particularly, preferred metal coordination complexes correspond to the formula I:

$$Cp^* \!-\! M \overset{\displaystyle Z'}{\underset{\displaystyle (X)_n}{\diagdown}} \qquad I$$

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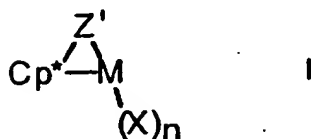
wherein:

M is a metal of Group 4, or the Lanthanide series of the Periodic Table of the Elements, especially a Group 4 metal, particularly titanium;

Cp* is a cyclopentadienyl group bound in an ^{5} bonding mode to M or

10   such a cyclopentadienyl group substituted with from one to four substituents selected from the group consisting of hydrocarbyl, silyl, germyl, halo, hydrocarbyloxy, amine, and mixtures thereof, said substituent having up to 20 nonhydrogen atoms, or optionally, two substituents together cause Cp* to have a fused ring structure;

15   Z' is a divalent moiety other than a cyclopentadienyl group or substituted cyclopentadienyl group, said Z' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z' together form a fused ring system;

20   X independently each occurrence is an anionic ligand group having up to 50 non-hydrogen atoms and X cannot be cyclopentadienyl or a substituted cyclopentadienyl group; and

n is 1 or 2 depending on the valence of M.

25   As noted above, M is preferably a Group 4 metal, especially titanium; n is 0, 1 or 2; and X is monovalent ligand group of up to 30 nonhydrogen atoms, more preferably, a C_{1-20} hydrocarbyl group. The term "substituted cyclopentadienyl" includes, for example, the indenyl and fluorenyl groups.

30   More preferably still, such metal coordination complexes correspond to the formula II:
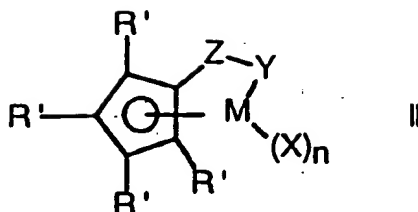
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wherein R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms or two R' groups together form a divalent derivative thereof;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms;

Y is a divalent ligand group selected from nitrogen, phosphorus, oxygen and sulfur and having up to 20 non-hydrogen atoms, said Y being bonded to Z and - M through said nitrogen, phosphorus, oxygen or sulfur, and optionally Y and Z together form a fused ring system;

M is a Group 4 metal, especially titanium;

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, BR^*, or BR^*_2; wherein:

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non- hydrogen atoms, and mixtures thereof, or two or more R* groups from Z, or from Z together with Y form a fused ring system; and

n is 1 or 2.

Preferably, Y is selected from -O-, -S-, $-NR^*-$, and $-PR^*-$. More preferably Y is a nitrogen or phosphorus containing group corresponding to the formula $-N(R')-$ or $-P(R')-$, wherein R' is as previously defined.

Most highly preferred metal coordination complexes correspond to the formula III:

$$\text{R'} \overset{\text{R'}}{\underset{\text{R'}}{\overset{\text{(ER'}_2)_m}{\underset{\text{R'}}{\bigcirc}}}} \overset{\text{N—R'}}{\underset{\text{(X)}_n}{\text{M}}} \qquad \text{III}$$
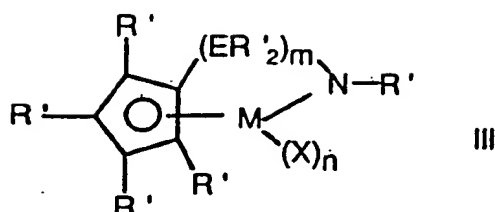
wherein:

M is titanium bound in an ^{5} bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms, or two R' groups together form a divalent derivative thereof;

E is silicon or carbon;

X independently each occurrence is selected from hydride, halo, alkyl, aryl, aralkyl, aryloxy and alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, (including all isomers of said propyl, butyl, pentyl, hexyl groups), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is a hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is a chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.

Specific highly preferred compounds include: (tert-butylamido)(tetra-methyl-^{5}-cyclopentadienyl)-1,2- ethanediyltitanium dimethyl, (tert-butylamido)(tetramethyl-^{5}- cyclopentadienyl)-1,2-ethanediyltitanium dibenzyl, (tert- butylamido)(tetramethyl-^{5}- cyclopentadienyl)dimethylsilanetitanium dimethyl, (tert- butylamido)(tetramethyl-^{5}- cyclopentadienyl)dimethylsilanetitanium dibenzyl, (methylamido)(tetramethyl-^{5}- cyclopentadienyl)dimethylsilanetitanium dimethyl,

(methylamido)(tetramethyl-5- cyclopentadienyl)dimethylsilanetitanium dibenzyl,
(phenylamido)(tetramethyl-5- cyclopentadienyl)dimethylsilanetitanium dimethyl,
(phenylamido)(tetramethyl-5- cyclopentadienyl)dimethylsilanetitanium dibenzyl,
(benzylamido)(tetramethyl-5- cyclopentadienyl)dimethylsilanetitanium dimethyl,
(benzylamido)(tetramethyl-5- cyclopentadienyl)dimethylsilanetitanium dibenzyl,
(tert- butylamido)(5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (tert-
butylamido)(5-cyclopentadienyl)-1,2- ethanediyltitanium dibenzyl, (tert-
butylamido)(5- cyclopentadienyl)dimethylsilanetitanium dimethyl, (tert-
butylamido)(5-cyclopentadienyl)dimethylsilanetitanium dibenzyl, (methylamido)(5-
cyclopentadienyl)dimethylsilanetitanium dimethyl, (t-butylamido)(5- cyclopenta-
dienyl)dimethylsilanetitanium dibenzyl, (t- butylamido)indenyldimethylsilane-
titanium dimethyl, (t- butylamido)indenyldimethylsilanetitanium dibenzyl,
(benzylamido)indenyldimethylsilanetitanium dibenzyl; and the corresponding
zirconium or hafnium coordination complexes.

The complexes may be prepared by contacting a metal reactant of the
formula: $MX_nX'_2$ wherein M, X, and n are as previously defined, and X' is a
suitable leaving group, especially halo, with a double Group I metal derivative or
double Grignard derivative of a compound which is a combination of the
delocalized -bonding group having the constrain inducing moiety, especially
C-Cp-Z'-L, where L is the Group I metal or Grignard, attached thereto. The
reaction is conducted in a suitable solvent and the salt or other byproduct is
separated. Suitable solvents for use in preparing the metal complexes are aliphatic
or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane,
heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene, ethylbenzene,
etc., or mixtures thereof. This technique is described in EP 0416815.

Ionic, active catalyst species, which are formed by combining (a) as
defined above and (b) as defined herein, preferably corresponding to the formula:
$$(CG^+)_d A^{d-}$$
wherein:
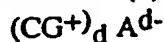
CG^+ is a cationic derivative of the previously defined metal coordination
complex;

A^{d-} is a noncoordinating, compatible anion having a charge of d, and

d is an integer from 1 to 3.

Preferred ionic catalysts correspond to the formula IV:
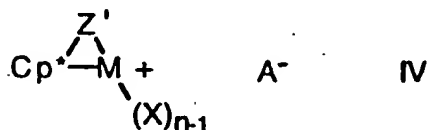
$$Cp^* \!-\! M \overset{\displaystyle Z'}{\underset{(X)_{n\text{-}1}}{\triangle}} + \qquad A^- \qquad IV$$

5

wherein:

Cp*, Z', M, X, and n are as defined with respect to previous formula I, and

A⁻ is a monovalent, noncoordinating, compatible anion.

10

More highly preferred ionic catalysts correspond to the formula V:

$$R' \!-\! \overset{R'}{\underset{R'}{\bigcirc}} \!\overset{Z-Y}{\underset{(X)_{n-1}}{M}} + \qquad A^- \qquad V$$

wherein:

R', Z, Y, M, X, and n are as defined with respect to previous formula II, and

15

A⁻ is a monovalent, noncoordinating, compatible anion.

Most highly preferred ionic catalysts correspond to the formula VI:

$$R' \!-\! \overset{R'}{\underset{R'}{\bigcirc}} \!\overset{(ER'_2)_m}{\underset{(X)_{n-1}}{M}}\!\!\overset{N-R'}{+} \qquad A^- \qquad VI$$

wherein:

R', E, M, N, m and n are as defined with respect to previous formula III,

20   and

A⁻ is a monovalent, noncoordinating, compatible anion.

One method of making these ionic catalysts involves combining:

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a$_1$) the previously disclosed metal coordination complex containing at least one substituent which will combine with the cation of a second component, and
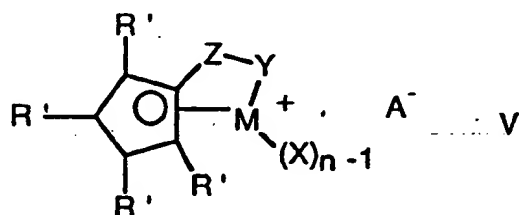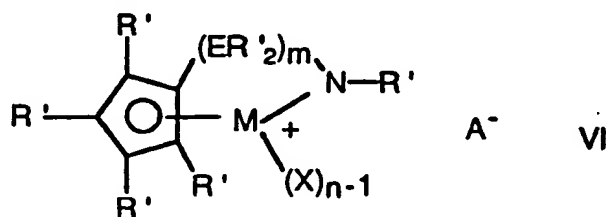
b$_1$) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

More particularly the noncoordinating, compatible anion of the Bronsted acid salt may comprise a single, non-nucleophilic, coordination complex comprising a charge-bearing metal or nonmetal core. Preferred anions comprise aluminum, silicon, boron, or phosphorus.

Preferred metal complexes for the foregoing reaction are those containing at least one hydride, hydrocarbyl or substituted hydrocarbyl group. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, or toluene.

Compounds useful as a second component (b) in the foregoing preparation of the ionic catalysts in step b$_1$) will comprise a cation, which is a Bronsted acid capable of donating a proton, and the anion A$^-$. Preferred anions are those containing a single coordination complex comprising a negative charge bearing core which anion is capable of stabilizing the active catalyst species (the metal cation) which is formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers, nitriles and the like. Compounds containing anions which comprise coordination complexes containing a single core atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

The second component useful in this preparation of the ionic catalysts used in this invention may be represented by the following general formula VII:

$$(L-H)_d^+ \, [A]^{d-} \qquad \text{VII}$$

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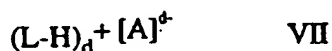
wherein:

L is a neutral Lewis base;

$(L-H)^+$ is a Bronsted acid; and

A^{d-} is as previously defined.

5   More preferably A^{d-} corresponds to the formula:

$$[M'^{m+}Q_n]^{d-}$$
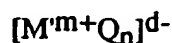
wherein:

10   m' is an integer from 1 to 7;

n' is an integer from 2 to 8;

n'-m' = d;

M' is an atom selected from Groups 5-13 of the Periodic Table of the Elements; and

15   Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide.

20   Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

$$[L-H]^+ [BQ_4]^-$$
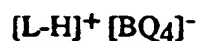
25   wherein:

L is a neutral Lewis base;

$[L-H]^+$ is a Bronsted acid;

30   B is boron in a valence state of 3; and

Q is a C_{1-20} fluorinated hydrocarbyl group. Most preferably, Q is each occurrence a perfluorinated aryl group, especially, tetrakis-pentafluorophenylborate.

Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl ammonium salts or triaryl ammonium salts such as: trimethylammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate,

5   trimethylammonium tetrakisperfluorophenylborate, triethylammonium tetrakisperfluorophenylborate, tripropylammonium tetrakisperfluorophenylborate, tri(n-butyl)ammonium tetrakisperfluorophenylborate, tri(t-butyl)ammonium tetrakisperfluorophenylborate, N,N-dimethylanilinium tetrakisperfluorophenylborate, N,N-diethylanilinium tetrakisperfluorophenylborate,

10   N,N-(2,4,6-pentamethyl)anilinium tetrakisperfluorophenylborate, trimethylammonium tetrakis- (2,3,4,6-tetrafluorophenylborate, N,N-dimethyl-anilinium tetrakis-(2,3,4,6-tetrafluorophenylborate, N,N-(2,4,6- penta-methyl)anilinium tetrakis-(2,3,4,6- tetrafluorophenylborate, and the like; dialkyl ammonium salts such as di-(i-propyl)ammonium tetrakis-pentafluorophenylborate,

15   dicyclohexylammonium tetrakis-pentafluorophenylborate and the like; and triaryl substituted phosphonium salts such as triphenylphosphonium tetrakis-pentafluorophenylborate, tri(o- tolyl)phosphonium tetrakis-pentafluorophenylborate, tri(2,6- dimethylphenyl)phosphonium tetrakis-pentafluorophenylborate, and the like.

20
        Another technique for preparing the ionic complexes involves combining:
        a_2) the previously disclosed metal coordination complex (first component); and
        b_2) at least one second component which is a salt of a carbenium and the

25   previously disclosed noncoordinating, compatible anion, A⁻.

        Another technique for preparing the ionic complexes involves combining:
        a_3) a reduced metal derivative of the desired metal coordination complex wherein the metal is in an oxidation state one less than that of the metal in the

30   finished complex; and
        b_3) at least one second component which is a salt of a cationic oxidizing agent and a noncoordinating, compatible anion.

        The second component useful in this preparation of the ionic catalyst used

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in this invention may be represented by the following general formula VIII:

$$(Ox^{e+})_d(A^{d-})_e \quad VIII$$

5   wherein:

Ox^{e+} is a cationic oxidizing agent having a charge of +e; and
A^{d-} is as previously defined.

Preferred cationic oxidizing agents include: ferrocenium, bisindenyl
10   Fe(III), cationic derivatives of substituted ferrocenium, Ag^+, Pd^{+2}, Pt^{+2}, Hg^{+2},
Hg_2^{+2}, Au^+, or Cu^+. Preferred embodiments of A^{d-} are those anions previously
defined, especially, tetrakisperfluorophenylborate.

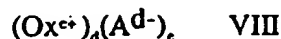A still further technique for preparing the ionic complexes involves
15   combining:

a_4) a reduced metal derivative of the desired metal coordination complex
wherein the metal is in an oxidation state one less than that of the metal in the
finished complex; and

b_4) at least one second component which is a neutral oxidizing agent in
20   combination with a Lewis acid mitigating agent. Suitable oxidizing agents are
quinone compounds, especially bisquinones. Suitable Lewis acid mitigating agents
include trisperfluorophenylborane.

A final technique for preparing the ionic complexes is an abstraction
25   technique involving combining:

a_5) the previously disclosed metal coordination complex (first
component); and

b_5) a Lewis acid having sufficient Lewis acidity to cause abstraction of an
anionic ligand of the metal coordination complex thereby forming a cationic
30   derivative thereof.

Preferred metal coordination complexes for the foregoing abstraction
reaction are those containing at least one hydride, hydrocarbyl or substituted
hydrocarbyl group able to be abstracted by the Lewis acid. A preferred Lewis acid

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is tris(perfluorophenyl)borane.

Ionic complexes resulting from the latter abstraction technique have a limiting charge separated structure corresponding to the formula IX:

$$CG'^+ (XL)^- \quad IX$$
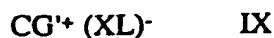
wherein:

CG' is the derivative formed by abstraction of an X group from the metal complex, which is as previously defined in it broadest, preferred and most preferred embodiments;

X is the anionic ligand abstracted from the metal coordination complex; and

L is the remnant of the Lewis acid. Preferably X is C_1-C_{10} hydrocarbyl, most preferably methyl.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:

$$CG''\text{--}X\bullet A$$
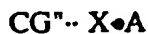
wherein CG" is the partially charge separated CG group.

Other catalysts which are useful as the catalyst compositions of this invention, especially compounds containing other Group 4 metals, will, of course, be apparent to those skilled in the art.

Component (c) of the invention is conveniently made by reacting SiO_2 and an aluminoxane. As will be apparent to those skilled in the art based upon the teachings herein, generally the higher surface area of the SiO_2 of component (c) the

better. Therefore, in general, the SiO_2 of component (c) is preferably a porous, fine particulate having a large surface area. Nevertheless, the particle size of the SiO_2 of component (c) will depend on whether the homogeneous three-component catalyst is to be used in a gas-phase polymerization process, a slurry polymerization

5   process, or a solution polymerization process.

Preferably, for use in an olefin polymerization process, the SiO_2 of component (c) has a porosity of from 0.2 to 1.5 cubic centimeter per gram (cc/g), more preferably from 0.3 to 1.2 cc/g, and most preferably from 0.5 to 1.0 cc/g,

10   each being a measure of the mean pore volume as determined by the BET technique using nitrogen as a probe molecule.

Preferably, for use in a gas-phase olefin polymerization process, the SiO_2 of component (c) has an mean particle diameter from about 20 microns to 200 microns, more preferably from 30 microns to 150 microns and most preferably

15   from 50 microns to 100 microns, each as measured by sieve analysis.

Preferably, for use in a slurry olefin polymerization process, the SiO_2 of component (c) has an mean particle diameter from about 1 microns to 150 microns, more preferably from 5 microns to 100 microns and most preferably from 20

20   microns to 80 microns, each as measured by sieve analysis.

Preferably, for use in a solution olefin polymerization process, the SiO_2 of component (c) has an mean particle diameter from 1 microns to 40 microns, more preferably from 2 microns to 30 microns and most preferably from 3 microns to 20

25   microns, each as measured by sieve analysis.

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The silica of component (c) is preferably dehydroxylated prior to reaction with aluminoxane. Dehydroxylation may be accomplished by any suitable means known in the art. A preferred means for the dehydroxylation reaction is heating of

5   a silica powder in a fluidized bed reactor, under conditions well known to those skilled in the art. Most preferably, conditions are chosen such that the silica is substantially dehydroxylated prior to reaction with aluminoxane but, it should be recognized that the silica need not be completely dehydroxylated.

10   Suitable commercially available silica for use in component (c) of the invention include precipitated silicas, available from the Davidson Division of W. R. Grace & Company in Connecticut.

The aluminoxane of component (c) is of the formula $(R^4_x(CH_3)_yAlO)_n$,

15   wherein R^4 is a linear or branched or C_3 to C_{10} hydrocarbyl, x is from 0 to 1, y is from 1 to 0, and n is an integer from 3 to 25, inclusive. The preferred aluminoxane components, referred to as modified methylaluminoxanes, are those wherein R^4 is a linear or branched C_3 to C_9 hydrocarbyl, x is from 0.15 to 0.50, y is from 0.85 to 0.5 and n is an integer between 4 and 20, inclusive; still more preferably R^4 is

20   isobutyl, tertiary butyl or n-octyl, x is from 0.2 to 0.4 , y is from 0.8 to 0.6 and n is an integer between 4 and 15, inclusive. Mixtures of the above aluminoxanes may also be employed in the practice of the invention.

Most preferably, the aluminoxane of component (c) is of the formula

25    $(R^4_x(CH_3)_yAlO)_n$, wherein R^4 is isobutyl or n-octyl, x is 0.75, y is 0.25 and n is from 6 to about 8.

Component (c) may be readily made by the reaction of SiO_2 and
aluminoxane in an inert solvent, under an inert atmosphere, preferably argon or
nitrogen, and under anhydrous conditions. Such reaction conditions are well
5   known. Suitable inert solvents include aliphatic or aromatic organic solvents.

Particularly preferred aluminoxanes are so-called modified aluminoxanes,
preferably modified methylaluminoxanes (MMAO), that are completely soluble in
alkane solvents, for example heptane, and include very little, if any,
10   trialkylaluminum. A technique for preparing such modified aluminoxanes is
disclosed in U.S. Patent No. 5,041,584. Aluminoxanes useful in preparing
component (c) of invention may also be made as disclosed in U.S. Patent Nos.
5,542,199; 4,544,762;, 5,015,749; and 5,041,585.

15   Use of aliphatic solvents is generally preferred in the preparation of
component (c) of the invention, since these solvents are generally readily removed
from the final polymerization product by devolatilization and they are thought to
present minimal, if any, health risks in either the manufacture of the polyolefin
product, in particular ethylene homopolymers and copolymers, or in the polyolefin
20   product itself. although, aromatic solvents, such as toluene, benzene, and the like,
can also be used in the preparation of component (c) of the invention, they are not
generally preferred.

A wide range of liquid aliphatic hydrocarbons can be used as solvents,
25   including mixtures of such hydrocarbons. This known class of compounds
includes, for example, pentane, hexane, heptane, isopentane, cyclohexane,

methylcyclohexane, isooctane, and the like, and mixtures of thereof, such as

commercial blends of C_8 to C_{10} alkanes sold under the tradename Isopar E by

Exxon Chemical Co. Most preferably, the solvent for making component (c) of the

invention is n-heptane.

5

While the order of addition of the SiO_2 and aluminoxane and solvent is not

thought to be critical in preparing component (c), it is generally preferred to add the

aluminoxane to a slurry of SiO_2 in the inert solvent. It is also preferred that the

SiO_2 and aluminoxane mixture be stirred throughout the reaction in order to

10   expedite the reaction process by providing and maintaining an intimate contact

between the reactants.

The reaction between SiO_2 and aluminoxane in making component (c) of

the invention may be performed a temperatures between about -20°C and about

15   120°C, preferably between about 0°C and about 100°C, more preferably between

about 20°C and about 80°C, and most preferably between about 40 and about

70°C, all preferably at about atmospheric pressure. The time of the reaction

between SiO_2 and aluminoxane may be from about 15 minutes (min) to about 24

hours, preferably from about 30 min to about 12 hours, more preferably from

20   about 1 hour to about 8 hours, and most preferably from about 2 hours to about 4

hours, in accordance with the conditions of temperature and pressure set forth

above.

The time and temperature required for the completion of the reaction

25   between SiO_2 and aluminoxane may readily be determined for any particular batch

of starting materials and solvents by monitoring evolution of gaseous by-products,

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the reaction being complete when no further by-product evolution occurs.

While it is most preferred that the SiO_2 of component (c) is reacted to saturation with an aluminoxane, less than full saturation of the SiO_2 is operable in the product and process of the invention; however, the resultant supported homogeneous catalyst is expected to operate at less than optimal efficiencies, and thus is not desired.

The supported homogeneous organometallic catalyst of the present invention is readily prepared by combining and reacting component (a), component (b) and component (c), in any order, after which the supported organometallic catalyst thereby obtained is introduced into a polymerization reactor vessel. Thus, component (a) may first be reacted with component (b), and component (c) is subsequently added to the reaction product of components (a) and (b). Alternatively, component (a) may be added to a mixture of components (b) and (c), and the resultant product of the reaction between components is added to the polymerization reactor. Preferably, component (a) is first reacted with component (c), and the reaction product is then mixed with the activator component (b), and the resultant activated supported catalyst is added to the polymerization reactor. In general, the catalyst composition of the invention can be prepared by combining components (a), (b) and (c) in a suitable solvent or diluent, typically a mixture of C_8 to C_{10} saturated hydrocarbons (e.g., Isopar E made by Exxon) at a temperature within the range of from -100° C to 300° C, preferably from 0° C to 200° C, and more preferably from 25° C to 150° C. After the addition of all three components to the reaction medium, the resulting activated catalyst may be isolated as a solid from the reaction mixture, such as by filtration. The isolated, activated supported

catalyst may then be added to the polymerization reactor, if so desired, especially for gas phase polymerization processes.

It has been found that the composition of component (a) and component (c) is surprisingly stable. For example, such a composition has been found to be essentially fully activatable by component (b) up to about one month after the mixing of components (a) and (c). Such a stability represents another advantage of the present invention, in that a batch mixture of components (a) and component (c) can be initially made, and shipped if necessary, and later be made into the active catalyst of the invention. As such, the processes using the supported catalyst complexes of the invention are expected to be more reproducible from batch to batch than was heretofore attainable.

In addition, the mixture of the activated catalyst containing all three components, or the solid, supported, activated catalyst isolated from the reaction mixture after all three components have been added, is also surprisingly stable.

In the practice of the invention, the mole ratio of component (b) to component (a) is from 0.01:1 to 100:1, preferably from 0.1:1 to 20:1, and more preferably from 0.5:1 to 10:1. The mole ratio of Al in component (c) to metal, M, in component (a) is from 0.1:1 to 10,000:1, preferably from about 1:1 to 500:1, and more preferably from 3:1 to about 100:1.

Hydrogen or other chain transfer agents (i.e., telogens) can also be employed in the polymerization of olefins in the practice of the invention to control the chain length of polymers. The class of materials which can be used to control

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chain length of olefinic polymers especially ethylene homopolymers and

copolymers during polymerization and methods of using such materials for that

purpose are known in the art. Generally, the molar ratio of hydrogen to olefin

monomer(s) is from 0 to 1; preferably from 0 to 0.1; and, most preferably from 0.

5   to about 0.05.

The polymerization reaction especially the polymerization of ethylene

homopolymers and copolymers in the practice of the present invention in a solution

polymerization process may be conducted under temperatures and pressures in such

10   combinations as to provide acceptable polymerization efficiencies and as well as the

desired molecular weight interpolymers. The useful ranges for these processes are

readily determined by those skilled in the art.

The solution polymerization especially the polymerization of ethylene

15   homopolymers and copolymers may be either a "high pressure" or "low pressure"

process. Suitable reactor pressures for a solution polymerization for the above

temperature ranges are from about atmospheric pressure to 1000 psig (6900 kPa),

preferably from 15 psig to 700 psig (100 kPa to 4800 kPa), and most preferably

from 200 psig to 600 psig.

20

As would be readily recognized by those skilled in the art, the useful

polymerization reaction temperatures and pressures for slurry polymerization and

gas-phase polymerization can be readily determined, and are generally those that are

known.

25

Suitable solvents or diluents in the polymerization reaction include those

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compounds known to be useful as solvents or diluents in the polymerization of

olefins and diolefins. Suitable solvents or diluents include, but are not meant to be

limited to, straight and branched chain hydrocarbons, preferably C_1 to C_{10}

hydrocarbons, such as isobutane, butane, pentane, isopentane, hexane, heptane,

5   octane, isooctane, nonane, and the like; cyclic and alicyclic hydrocarbons, such as

cyclohexane, cycloheptane, methyl cyclohexane, methylcycloheptane, and the like.

Suitable solvents or diluents also include liquid olefins which may act as

monomers or comonomers in the polymerization reaction, such as ethylene,

10   propylene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-

octene, 1-decene, styrene, and the like.

The polymerization reaction may be performed by any of the conventional

polymerization means which had been used for Ziegler Natta catalyzed reactions.

15   These include single phase systems wherein the single phase is primarily the

principal monomer or an inert diluent. Alternatively, a two-phase polymerization

system may be employed where the liquid phase is primarily the principal monomer

or an inert diluent. The catalyst compositions of the present invention are

particularly suitable for gas-phase or slurry polymerization reaction systems.

20

In a preferred embodiment, the supported catalyst composition of the

invention is used either to homopolymerize ethylene or to copolymerize ethylene

(the most preferred principal monomer) with -olefin comonomers having from 3 to

20 carbon atoms, preferably from 3 to 18 carbon atoms, more preferably from 3 to

25   12 carbon atoms, and most preferably from 3 to 10 carbon atoms, including

styrene, thereby yielding a copolymer. Copolymers of propylene with either

- 30 -

ethylene, with either as principal monomer or on an equimolar basis, or copolymers with propylene as principal monomer and C_4 to C_{20}, preferably C_4 to C_{18}, more preferably C_4 to C_{12} and most preferably C_4 to C_{10}, alpha-olefin comonomers are also preferred. As would be readily apparent to those skilled in the art, polyolefin

5   copolymers comprising more than two chemically distinct monomeric units (e.g., terpolymers, etc.) may also be conveniently made in the practice of the invention. It is therefore to be understood that "copolymer", as used herein, is meant to include any polymer comprised of two or more chemically distinct monomeric units.

10

Preferred monomers include the C_2-C_{10} -olefins especially ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes,
tetrafluoroethylene, vinylbenzocyclobutene, 1,4-hexadiene, and naphthenics (e.g.,
15   cyclopentene, cyclohexene and cyclooctene).

The molecular weight of the ethylene or ethylene/-olefin substantially linear olefin polymers in the present invention is conveniently represented by I_2, as described in ASTM D-1238. Throughout this disclosure, "melt index" or "I_2" is
20   measured in accordance with ASTM D-1238 (190°C/2.16 kg); "I_{10}" is measured in accordance with ASTM D-1238 (190°C/10 kg). For linear polyolefins, especially linear polyethylene, it is well known that as Mw/Mn increases, I_{10}/I_2 also increases. With the ethylene or ethylene/-olefin substantially linear olefin polymers of this invention, the I_{10}/I_2 may be increased without increasing Mw/Mn. The melt
25   index for the ethylene or ethylene/-olefin substantially linear olefin polymers used herein is generally from 0.01 grams/10 minutes (g/10 min) to 1000 g/10 min, preferably from 0.01 g/10 min to 100 g/10 min, and especially from 0.01 g/10 min to 10 g/10 min.

30   The copolymers have a I_{10}/I_2 melt flow ratio of from 6 to 18, and preferably from 6 to 14.

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The density of the ethylene or ethylene/-olefin substantially linear olefin
polymers in the present invention is measured in accordance with ASTM D-792 and
is generally from 0.85 g/cm^3 to about 0.96 g/cm^3, preferably from 0.865 g/cm^3 to

5   0.96 g/cm^3. The density of the copolymer, at a given melt index level for the
copolymer, is primarily regulated by the amount of the comonomer which is
copolymerized with the ethylene. In the absence of the comonomer, the ethylene
would homopolymerize with the catalyst of the present invention to provide
homopolymers having a density of about >0.95. Thus, the addition of

10   progressively larger amounts of the comonomers to the copolymers results in a
progressive lowering of the density of the copolymer. The amount of each of the
various -olefin comonomers needed to achieve the same result will vary from
monomer to monomer, under the same reaction conditions. Thus, to achieve the
same results, in the copolymers, in terms of a given density, at a given melt index

15   level, larger molar amounts of the different comonomers would be needed in the
order of $C_3>C_4>C_5>C_6>C_7>C_8$.

Preferably, the polymerization temperature is from about 0°C to about
110°C, using constrained geometry catalyst technology. If a narrow molecular
weight distribution polymer (M_w/M_n of from 1.5 to 2.5) having a higher I_{10}/I_2

20   ratio (e.g. I_{10}/I_2 of 7 or more, preferably at least 8, especially at least 9) is desired,
the ethylene partial pressure in the reactor is reduced. Generally, manipulation of
I_{10}/I_2 while holding M_w/M_n relatively low for producing the novel polymers
described herein is a function of reactor temperature and/or ethylene and

25   comonomer concentration.

The term "substantially linear" polymers means that the polymer backbone
is substituted with 0.01 long chain branches/1000 carbons to 3 long chain
branches/1000 carbons, more preferably from about 0.01 long chain branches/1000

30   carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long
chain branches/1000 carbons to 1 long chain branches/1000 carbons.

The term "linear olefin polymers" means that the olefin polymer has no long
chain branching, as for example the traditional linear low density polyethylene

polymers (including the sub-set of polymers known as very low density polyethylene (VLDPE) or alternatively known as ultra low density polyethylene (ULDPA)) or linear high density polyethylene polymers which are heterogeneously branched polymers made using Ziegler polymerization processes (e.g., USP

5   4,076,698 or USP 3,645,992, which are incorporated herein by reference). The term "linear olefin polymers" does not refer to high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers which are known to those skilled in the art to have numerous long chain branches.

10

Long chain branching is defined herein as a chain length of at least 6 carbons found in ethylene homopolymers, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer back-

15   bone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method of Randall (Rev. Macromol.Chem. Phys., C29 (2&3), p. 285-297).

20

"Melt tension" is measured by a specially designed pulley transducer in conjunction with the melt indexer. Melt tension is the load that the extrudate or filament exerts while passing over the pulley at the standard speed of 30 rpm. The melt tension measurement is similar to the "Melt Tension Tester" made by

25   Toyoseiki and is described by John Dealy in "Rheometers for Molten Plastics", published by Van Nostrand Reinhold Co. (1982) on page 250-251.

The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the

30   polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p.

441 (1982), or in U.S. Patent 4,798,081. The SCBDI or CDBI for the new polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent. These resins are characterized in that they have a single melting point as determined using Differential Scanning Calorimetry (DSC).

A unique characteristic of the presently claimed polymers is a highly unexpected flow property where the I_{10}/I_2 value is essentially independent of polydispersity index (i.e. M_w/M_n). This is contrasted with conventional polyethylene resins having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

The whole interpolymer product samples and the individual interpolymer samples are analyzed by gel permeation chromatography (GPC) on a Waters 150°C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3, 10^4, 10^5, and 10^6), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is 200 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, to derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w = R\ w_i * M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the ith fraction eluting from the GPC column.

Processing Index Determination

The rheological processing index (PI) is measured by a gas extrusion
rheometer (GER). The GER is described by M. Shida, R.N. Shroff and L.V.
Cancio in Polym. Eng. Sci., Vol. 17, no. 11, p. 770 (1977), and in "Rheometers
for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co.
(1982) on page 97-99. The processing index is measured at a temperature of
190°C, at nitrogen pressure of 2500 psig using 0.0296 inch diameter, 20:1 L/D die
having an entrance angle of 180°. The GER processing index is calculated in
millipoise units from the following equation:

$$PI = 2.15 \times 10^6 \text{ dynes/cm}^2 / (1000 \times \text{shear rate}),$$

where: 2.15×10^6 dynes/cm^2 is the shear stress at 2500 psi, and the shear
rate is the shear rate at the wall as represented by the following equation:

$$32 \text{ Q'/ } (60 \text{ sec/min})(0.745)(\text{Diameter} \times 2.54 \text{ cm/in})^3, \text{ where:}$$

Q' is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm^3), and

Diameter is the orifice diameter of the capillary (inches).

The PI is the apparent viscosity of a material measured at apparent shear stress of
2.15×10^6 dyne/cm^2.

For the substantially linear olefin polymers disclosed herein, the PI is less
than or equal to 70 percent of that of a comparative linear olefin polymer at about
the same I_2 and M_w/M_n.

An apparent shear stress vs. apparent shear rate plot is used to identify the
melt fracture phenomena. According to Ramamurthy in Journal of Rheology,
30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate
irregularities may be broadly classified into two main types: surface melt fracture
and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and
ranges in detail from loss of specular gloss to the more severe form of "sharkskin".
In this disclosure, the onset of surface melt fracture is characterized at the beginning

of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

The polyolefins especially ethylene homopolymers and copolymers of the invention may be used to prepare fabricated articles using conventional polyolefin processing techniques. Useful fabricated articles include those such as films (e.g., cast, blown and extrusion coated), fibers (e.g., staple fibers, spunbond fibers or melt blown fibers) and gel spun fibers, both woven and non-woven fabrics (e.g., spunlaced fabrics), and articles made from blends of such fibers, as well as molded articles made, for example, by conventional injection molding, blow molding and rotomolding processes.

In order that persons skilled in the art may better understand the practice of the present invention, the following examples are provided by way of illustration, and not by way of limitation. Additional information which may be useful in state-of-the-art practice may be found in each of the references and patents cited herein.

Example 1

A.   Preparation of (Tert-butylamido)dimethyl(tetramethyl-n^5-cyclo-

pentadienyl)silanetitanium dimethyl Catalyst Complex.

In a drybox, 4.0 mL of 2.0 M isopropylmagnesium chloride in diethyl ether

was syringed into a 100 mL flask. The ether was removed under reduced pressure

to leave a colorless oil. 20 mL of a 4:1 (by volume) toluene:tetrahydrofuran (THF)

mixture was added followed by 0.97 g of (tert-butylamino)dimethyl(tetramethyl-

cyclopenta-dienyl)silane. The solution was heated to reflux. After 8-10 hours, a

white precipitate began to form. After refluxing for a total of 27 hours, the solution

was cooled and the volatile materials were removed under reduced pressure. The

white solid residue was slurried in pentane and filtered to leave a white powder

(1.23 g, 62% yield) of $[Me_4C_5SiMe_2N\text{-}t\text{-}Bu]Mg_2Cl_2(THF)_2$ (where Me is

methyl, t-Bu is tertiary butyl and THF is tetrahydrofuran).

In the drybox, 0.10 g of $TiCl_3(THF)_3$ was suspended in 40 mL of THF.

0.138 g of solid $[Me_4C_5SiMe_2N\text{-}t\text{-}Bu]Mg_2Cl_2(THF)_2$ was added, resulting in a

color change from pale blue to deep purple, signifying the formation of the complex

(tert- butylamido)dimethyl(tetramethyl-n^{5}cyclo-pentadienyl)silanetitanium chloride.

After stirring for 5 minutes, 0.17 mL of a 1.56 M solution of methylene chloride in

tetrahydrofuran was added. The color changed to bright yellow. After several

minutes the THF was removed under reduced pressure. The product was recovered

by extraction in pentane. The yield was 70 percent. The product's identity was

confirmed as (tert-butylamido)dimethyl-(tetramethyl- n^5-cyclopentadienyl)-

silanetitanium dichloride by ^{1}H NMR, (C_6D_6): 1.992 (s), 1.986 (s), 1.414 (s),

0.414 (s).

In an inert atmosphere box, 9.031 g of (tert-butylamido)dimethyl-
(tetramethyl- n^5-cyclopentadienyl)-silanetitanium dichloride is charged into a 250
5   mL flask and dissolved into 100 mL of THF. To the solution is added 35 mL of a
1.4 M methylmagnesium bromide solution in toluene/THF. The reaction mixture is
stirred for 20 min follwed by removal of the solvent under vacuum. The resulting
solid is dried under vacuum for several hours. The product is extracted with
pentane and filtered. The pentane is removed from the filtrate under vacuum
10   leaving the complex as a yellow solid.

B.   Preparation of Borane Activator, Tris(pentafluorophenyl)borane.

The borane activator (component (b)) was prepared by the reaction of the
Grignard reagent C_6F_5MgBr with BF_3 etherate in diethylether. After the reaction
15   was complete, the ether solvent was removed under vacuum, the product extracted
with Isopar E, the extracts filtered to yield a solution of the borane for use as
component (b).

C.   Preparation of Silica-Aluminoxane

20

A 500 mL flask was charged with 5.0g of SiO_2 (Davison® Syloid 245),
which had been dehydroxylated in a fluidized bed in nitrogen at 600° C for 12
hours. A volume of hydrocarbon solvent, Isopar E, was then added to the silica to
generate a slurry. A sample of 20 mL of a 6.2 weight percent solution of modified
25   methylaluminoxane (Akzo Chemical) in heptane was slowly added to the slurry by
syringe over the course of about 5 minutes. The resultant mixture was heated at

about 75° C for about 3 hours under nitrogen, followed by cooling to room

temperature.

The flask was next transferred to an inert atmosphere box (nitrogen

5   atmosphere) and the solid in the flask collected on a medium porosity fritte and

washed with Isopar E. After drying under nitrogen gas, the resultant white solid

was transferred to an 8 oz. bottle and suspended in about 250 mL Isopar E

solvent. The suspension was found to contain a silica concentration of 20 g/L and

an aluminum content of 0.100 M. The ratio of aluminum to silica in the sample

10   was determined to be 5.0 mmole/g (Al:SiO$_2$).

D.   Formation of the Supported Homogeneous Catalyst Complex

The (tert-butylamido)dimethyl(tetramethyl-5-cyclo-pentadienyl)silane

dimethyltitanium complex was dissolved in Isopar E to give a clear solution of Ti

15   concentration of 5 mM. Fifty mL of this solution (0.25 mmole Ti) was added to

150 mL of the above-described slurry of silica-aluminoxane in a 16 oz. bottle and

the solution was stirred for about 70 hours. The supernatant fluid was decanted

from the solids to remove any unsupported compounds. The solids were then

resuspended in 65 mL of Isopar E. The solids were determined to contain 0.054

20   mmole Ti/g SiO$_2$.

E.   Catalyst Activation

A sample of the above reaction mixture containing 0.005 mmol Ti was

25   transferred to a 4 oz bottle. The slurry was treated with 2.0 mL of component (b)

from above (0.020 mmol component (b)) for 2 minutes at 25 ° C with stirring, and

the reaction product containing the activated, supported homogeneous catalyst complex slurried in the liquid hydrocarbon was transferred by syringe to the catalyst injection port on a batch polymerization reactor.

5   Example 2

Solution Polymerization

A stirred, one gallon (3.79 L) autoclave reactor was charged with two liters of Isopar E and 175 mL of octene-1, before heating to reaction temperature. The

10   reactor was then charged with 4 mmol hydrogen gas followed by ethylene sufficient to bring the total pressure in the reactor to 450 psig. The slurry of the activated catalyst, as prepared in Example 1, was next injected into the reactor. The reaction temperature and pressure were kept essentially constant at 120° C and 450 psig, by continually feeding ethylene during the polymerization reaction and

15   cooling the reactor as necessary. The rate and duration of the reaction were monitored by measuring the demand flow of ethylene to the reactor for the polymerization. The yield was about 235 g polyethylene (47,000 g polyethylene/mmol Ti added to the reactor) based on the amount of polymer isolated from the polymerization solution. The copolymer had a melt index of 3.4,

20   an I_{10}/I_2 ratio of 6.5, and a density of 0.9084 g/cc.

Example 3

Slurry Polymerization

25   A 5 L autoclave reactor was charged with about 1850 g anhydrous hexane with stirring and the reactor contents heated to about 85° C. The reactor pressure

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`was then increased by 5 psig by the addition of hydrogen gas to the reactor headspace, followed by a sufficient quantity of ethylene to raise the total pressure to 175 psig. A sample of activated catalyst complex containing about 0.002 mmol Ti, prepared essentially according to Example 1, was next added to the reactor through a pressurized addition cylinder. Ethylene was supplied to the reactor continuously using a demand feed regulator on the feed line. After about 45 minutes, the ethylene was blocked in and the reactor vented and cooled. The reactor contents were padded to a filter system where the polymer was removed from the hexane and dried under vacuum overnight. The yield of free-flowing, granular polyethylene thus obtained weighed 38.4 g and the product showed a melt flow rate (I_2) of 0.70 g/10 min and a melt flow rate (I_{10}) of 4.68 g/10 minutes.

Example 4

A.   Catalyst Preparation

The organometallic complex and borane activator were prepared essentially as set forth in the Example above. The supported homogeneous catalyst was prepared as follows:

A 500 mL flask was charged with about 50 mL of toluene and about 5.0 g of SiO_2 (Davidson Syloid 245), that had been dehydroxylated at about 600° C for about 12 hours in a fluidized bed under nitrogen. Fifty mL of methylaluminoxane (0.991 M aluminum; 50 mmol Al) were slowly added by syringe into the slurry with stirring. The resultant mixture was then heated for about 3 hours at 60° C under a nitrogen atmosphere, after which the mixture was cooled to room

temperature. The flask was then transferred to an inert atmosphere box (nitrogen) and the solid collected on a medium porosity fritte and washed 3 times with 30 mL toluene followed by 5 washes with Isopar E. After drying under nitrogen, the white solid was transferred to an 8 oz. bottle and suspended in about 200 mL

5   Isopar E. The suspension was determined to contain silica at about 25 g/L and the aluminum content was found to be about 0.063 M.

A sample of the above reaction mixture containing a known amount of aluminum was transferred to a 4 oz. bottle. The slurry was treated with an Isopar E

10   solution of catalyst complex (component (a)) containing a specified amount of Ti and component (c) containing a specified amount of borane. The activation reaction was carried out essentially as described above, after which the reaction product was transferred by syringe to the catalyst injection port on the polymerization reactor.

15   Examples 5 to 15 - Solution Polymerizations

The solution polymerization were carried out essentially as described in Example 2 above, with the exception that the reactor was charged with 150 mL octene-1 and 10 mmol hydrogen, and the components in Example 4 were used.

20   Table 1 summarizes the polymerization reaction conditions and certain characteristics of the polyethylene product obtained. Additionally, in reaction 12, the reactor was charged with 300 mL octene-1 and no hydrogen was added, and in Example 13, only 4 mmol of hydrogen was charged into the reactor. Furthermore, in Example 14 the supported homogeneous catalyst complex was (tert-

25   butylamido)dimethyl(tetramethyl-5-cyclopentadienyl)silane dibenzyltitanium. In Example 15, the supported homogeneous catalyst complex was the

tetrahydroindenyl derivative (C9H10-Me2Si-N-t-Bu)Ti(CH3)2.

Example 6 is a comparative example without a boron activator.

5   TABLE 1

Example No.	Reactor Temp. (°C)	Ti (m mol)	B (m mol)	Al (m mol)	Yield (g)	I_2	I_{10}/I_2	Density (g/cc)
5	120	5	10	63	176	2.76	6.14	0.9121
6	120	5	0	63	0			
7	120	5	10	32	135	5.97	5.85	0.9094
8	120	5	10	95	278	5.82	6.12	0.9099
9	120	5	10	126	345	6.69	6.30	0.9083
10	120	5	10	158	325	7.26	6.21	0.9090
11	120	5	10	126	260	6.43	6.41	0.9062
12	120	5	10	126	310	5.61	7.35	0.8785
13	120	5	10	126	288	2.60	6.74	0.9048
14	120	5	10	126	212	2.97	6.03	0.9077
15	120	5	10	126	233	1.51	6.94	0.8882

<u>Example 16 - Catalyst Preparation</u>

10

Solutions of the Ti organometallic complex component (a)

and the borane activator component (b) were prepared essentially as described in

Example 1.

15   Component (c). A 500 mL flask was charged with 5.0 g SiO2 (Davidson 952

Silica, dehydroxylated at about 600°C for greater than 18 hours) and 50 mL Isopar

E. To this stirred slurry was added slowly by syringe 20 mL of a 6.2 weight

percent solution of modified methylaluminoxane (Akzo Chemical) in heptane

dissolved in 30 mL Isopar E. The resulting mixture was next heated at about 75° C

20   for about 3 hours under nitrogen, and subsequently cooled to room temperature.

The flask was transferred to an inert atmosphere (nitrogen) box and the solid

collected on a medium porosity fritte and washed with Isopar E. After drying
under nitrogen, the white solid was transferred to an 8 oz. bottle and suspended in
about 250 mL Isopar E solvent. The suspension was determined to contain a silica
concentration of about 20 g/L and an aluminum content of about 0.065 M. The
ratio of aluminum to silica in the sample was about 3.0 mmol Al/g SiO_2.

Catalyst Activation. A sample of the preceding SiO_2-aluminoxane reaction product
containing a known amount of Al was transferred to a 4 oz. bottle. The slurry was
treated with an Isopar E solution of component (a) containing a specified amount of
Ti and component (b) containing a specified amount of borane. The activated,
supported organometallic catalyst complex was transferred to a polymerization
reactor via syringe injection through a catalyst injection port.

Examples 17 to 19 - Solution Polymerizations

The following polymerizations were conducted according to the procedure set
forth in Example 2, with the exception that the reactor was charged with 150 mL
octene and the components in Example 16 were employed. The reaction conditions
and characterization of the ethylene-octene copolymers produced are summarized in
Table 2.

TABLE 2

Example No.	Reactor Temp. (°C)	Ti (m mol)	B (m mol)	Al (m mol)	Yield (g)	I_2	I_{10}/I_2	Density (g/cc)
17	140	5	10	65	102	2.44	5.79	0.9085
18	140	5	10	65	65	1.44	5.65	0.9124
19	140	5	10	65	110	1.90	5.93	0.9093

Example 20. Catalyst Preparation

Solutions of the Ti organometallic complex component (a)
and the borane activator component (b) were prepared essentially as described in
5   Example 1.

A 100 mL flask was charged with 1.0 g of SiO_2 (Davison Syloid 245,
dehydroxylated at 600°C) and 20 mL of Isoparaffin 2025 (an isoparaffinic
hydrocarbon solvent available from Shell Chemical). Five mL of MMAO in
10   heptane (8.6 wt% Al, Modified Methylaluminoxane from Akzo, Type 3A)
dissolved in 10 mL of Isoparaffin 2025 was added slowly, by syringe, to the
stirred SiO_2 slurry. The mixture was heated to 75°C for 3 hours then cooled to
room temperature and allowed to stir overnight. The solid was collected on
Whatman 541 filter paper and washed with an additional 10 mL of Isoparaffin
15   2025. The solid was not taken to complete dryness. The wet solid was transferred
to a 4 oz. bottle and suspended in 50 mL of Isoparaffin 2025.

Ten mL of this solution of component (a) was added to the silica slurry and
the mixture was stirred for 48 hours. After this time, the slurry was allowed to
20   settle and the supernatant was removed from the solids using a pasteur pipette. The
solids were reconstituted to a total volume of 50 mL with Isoparaffin 2025.

The catalyst was activated by adding a solution of component (b) containing
0.2 mmol of $(F_5C_6)_3B$ to the slurry and stirring vigorously overnight.

25

Example 21. Gas Phase Polymerization

A one-liter cylindrical reactor specifically designed for gas phase
polymerizations was charged with 30 g of Teflon powder (450 micron) to act as a
support bed. The reactor was then sealed and placed under vacuum at 90 °C for 18
5   h. The reactor was cooled to 70 °C and filled with nitrogen to a pressure of 20
psig. The Teflon bed was agitated at about 400 rpm and a 4 mL volume of 0.050
M MMAO in heptane was injected into the reactor by syringe. After about one
minute, 1.5 cc of the activated catalyst of Example 20 was injected into the reactor
from a syringe. Ethylene was then slowly added to the reactor to give an ethylene
10   partial pressure of 200 psig and the pressure maintained at the total pressure by
feeding ethylene on demand. After 3 hours, the ethylene was blocked in and the
reactor and its contents cooled to room temperature. The granular polyethylene
product was removed from the reactor and weighed, giving a yield of 52.4 g of
polyethylene. The product was analyzed by GPC and found to have an Mn value
15   of 1,320,000.

Example 22. Catalyst Preparation.

A. Preparation of (Tert-butylamido)dimethyl(tetramethyl-η^5-cyclo-
20   pentadienyl)silane 2-(dimethylamino)benzyl titanium(III) Catalyst Complex.

The complex (tert-butylamido)dimethyl(tetramethyl-η^5cyclo-
pentadienyl)silanetitanium(III) chloride was prepared in tetrahydrofuran according
to Example 1. This complex was treated with one equivalent of the lithium salt of
dimethylaminotoluene at room temperature for 30 minutes. The solvent was
25   evaporated and the solid residues extracted with pentane and the extracts filtered to
remove salt by-products. The pentane solvent was removed from the extract filtrate

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to yield the desired titanium(III) complex.

B.   Preparation of the Supported Homogeneous Catalyst Complex.

5   A supported catalyst complex was prepared substantially as in Example 1
except that the silica had been dehydroxylated at 800 °C for 8 h and the
titanium(III) complex above was used as the organometallic compound. The final
catalyst component slurry contained a Ti concentration of 1.25 millimolar.

10   ### C.   Catalyst Activation.

An activated catalyst complex was formed by mixing, in a 4 oz bottle, 3.2 mL
of the catalyst component slurry prepared above and 1.2 mL of a solution of the
borane activator from Example 1(b) at room temperature for 3 min.

15

Example 23. Solution Polymerization

The catalyst prepared in Example 22 was employed in a ethylene octene-1
copolymerization under solution process conditions similar to those described in
20   Example 2 except that the reactor temperature was maintained at 140 °C during the
polymerization. The ethylene-octene-1 copolymer recovered from the
polymerization reaction weighed 236 g (59,000 g polyethylene/mmol Ti), had a
melt index of 1.2, an ratio I_{10}/I_2 of 6.8, and a density of 0.9072 g/cc.

Example 24. Catalyst Preparation.

The titanium complex and the silica-aluminoxane mixture were prepared as
described in Example 1. The borate activator mixture was prepared as a slurry by
5   suspending [N,N-dimethylanilinuim][tetrakis(perfluorophenyl)borate] in Isopar E
in an amount of 0.01 moles/liter. The supported homogeneous catalyst complex
prepared in Example 1D was activated by mixing 5.0 mL of the reaction product
from Example 1D with (0.005 mmol B) with this borate activator mixture and
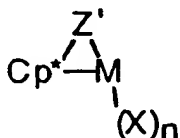stirring at 25°C for 10 minutes.

10

Example 25. Solution Polymerization

The polymerization was conducted essentially as set forth in Example 2 except
that the reaction temperature was kept at 140°C.   The yield was about 197 g
15   polyethylene (39,400 g polyethylene/mmol Ti added to the reactor) based on the
amount of polymer isolated from the polymerization solution. The polymer had a
melt index of 5.8, an I_{10}/I_2 ratio of 7.4, and a density of 0.9125 g/cc.

WHAT IS CLAIMED IS:

1.   An activated, supported homogeneous catalyst complex suitable for homopolymerizing ethylene or copolymerizing ethylene with at least one C_3 to C_{18} -olefin monomer to form an ethylene polymer having a narrow molecular weight distribution, said catalyst complex comprising:

(a)   an organometallic complex of the formula I:

$$Cp^*\!-\!\!\!\overset{\displaystyle \overset{Z'}{\diagup\!\!\diagdown}}{\underset{\displaystyle (X)_n}{M}}$$

wherein:

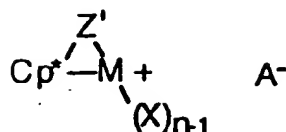M is a metal of Group 4 of the Periodic Table of the Elements,

Cp^* is a cyclopentadienyl group bound in an ^{5} bonding mode to M or such a cyclopentadienyl group substituted with from one to four substituents selected from the group consisting of hydrocarbyl, silyl, germyl, halo, hydrocarbyloxy, amine, and mixtures thereof, said substituent having up to 20 non-hydrogen atoms, or optionally, two substituents together cause Cp^* to have a fused ring structure;

Z' is a divalent moiety other than a cyclopentadienyl group or substituted cyclopentadienyl groups, said moiety having up to 20 non-hydrogen atoms, and optionally Cp^* and Z' together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 50 non-hydrogen atoms and X is not a cyclopentadienyl or substituted cyclopentadienyl group; and

n is 1 or 2 depending on the valence of M;

(b)   a compound or complex capable of converting the organometallic complex (a) into a cationic complex of the formula II:

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$$\underset{(X)_{n-1}}{\overset{Z'}{\underset{|}{Cp^*\!-\!M}}} + \qquad A^-$$

wherein:

Cp*, Z', M, X, and n are as defined above, and

A⁻ is a monovalent, noncoordinating, compatible anion, and

(c)   a catalyst support in contact with (a) and (b), said catalyst support comprising silica reacted with a methylaluminoxane, a modified methylaluminoxane, or a mixture thereof.

2.   The catalyst according to Claim 1 characterized in that Z' comprises boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally nitrogen, phosphorus, sulfur or oxygen,

3.   The catalyst according to Claim 1 characterized in that M is titanium, zirconium or hafnium; X is a monovalent ligand group of up to 30 nonhydrogen atoms, and n is 1 or 2.

4.   The catalyst according to Claim 2 wherein X is a C_{1-20} hydrocarbyl group.

5.   The catalyst of Claim 1, wherein said catalyst complex comprises:

a) a coordination complex corresponding to the formula:
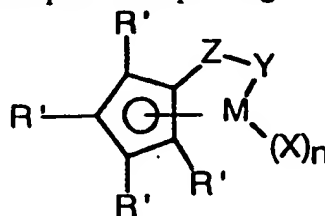
$$\begin{array}{c} R' \\ R'\!-\!\!\!\bigcirc\!\!\!-\!\!M\overset{Z-Y}{\underset{(X)_n}{}} \\ R' \quad R' \end{array}$$

wherein:

R' each occurrence is independently selected from the group consisting

- 50 -

of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof, having up to 20 non-hydrogen atoms;

Y is a divalent ligand group comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, said Y being bonded to Z and M through said nitrogen, phosphorus, oxygen or sulfur, and optionally Y and Z together form a fused ring system;

M is a Group 4 metal,

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, BR^*, or BR^*_2;

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non- hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or from Z together with Y forms a fused ring system;

n is 1 or 2; and

b) an activating cocatalyst selected from the group consisting of aluminoxanes, Lewis acids, and noninterfering oxidizing agents.

6.   The catalyst according to Claim 4 wherein Y is -O-, -S-, $-NR^*-$, $-PR^*-$ and R' is independently a C_{1-10} hydrocarbyl group.

7.   The catalyst according to Claim 5 wherein the activating cocatalyst is an alkylcycloborane, trisperfluorophenylborane or a mixture thereof.

8.   The catalyst composition according to Claim 1, wherein said aluminoxane is methylaluminoxane.

9.   The catalyst composition according to Claim 1, wherein said aluminoxane is modified methylaluminoxane.

10. In a supported catalyst composition suited for homopolymerization of ethylene or copolymerization of ethylene with a C_3 to C_{18} -olefin, said supported catalyst composition being characterized by a silica support reacted with a modified methylaluminoxane of the formula:

$$(R^4{}_x(CH_3)_yAlO)_n$$

wherein R^4 is a linear, branched or cyclic C_3 to C_{10} hydrocarbyl, x is ≥0 to about 1, y is from about 1 to 0, and n is an integer of from 3 to 25.

11. The catalyst support according to claim 9, wherein R^4 is a linear or branched C_3 to C_9 hydrocarbyl, x is from 0.15 to 0.50, y is from 0.85 to 0.5 and n is an integer of from 4 to 20.
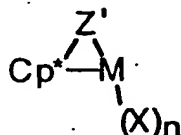
12. The catalyst support according to claim 10, wherein R^4 is selected from isobutyl, tertiary butyl and n-octyl, x is from 0.2 to 0.4, y is from 0.8 to 0.6 and n is an integer of from 4 to 15.

13. The catalyst support according to claim 11, wherein R^4 is isobutyl or n-octyl, x is about 0.75, y is about 0.25 and n is from 6 to 8.

14. A process for polymerizing an olefin, diolefin, or mixture thereof comprising contacting an olefin, diolefin, or mixture thereof with a catalyst composition according to any of the preceding Claims 1-9 under polymerization reaction conditions to polymerize said olefin, diolefin, or mixture thereof, and recovering the resulting polymer.

15. A process for preparing a supported catalyst composition comprising the steps of:

(a) preparing a organometallic complex of the formula I:

$$Cp^*—\overset{\overset{\textstyle Z'}{\diagdown}}{\underset{(X)_n}{\diagup}}M$$

wherein:

M is a metal of Group 4 of the Periodic Table of the Elements,

Cp* is a cyclopentadienyl group bound in an ^{5} bonding mode to M or such a cyclopentadienyl group substituted with from one to four substituents selected from the group consisting of hydrocarbyl, silyl, germyl, halo, hydrocarbyloxy, amine, and mixtures thereof, said substituent having up to 20 nonhydrogen atoms, or optionally, two substituents together cause Cp* to have a fused ring structure;

Z' is a divalent moiety other than a cyclopentadienyl group or substituted cyclopentadienyl groups, said Z' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z' together form a fused ring system;

X independently each occurrence is an anionic ligand group having up to 50 non-hydrogen atoms and X is not a cyclopentadienyl or substituted cyclopentadienyl group; and

n is 1 or 2 depending on the valence of M;

(b) reacting (a) with a compound or complex capable of converting the organometallic complex (a) into a cationic complex of the formula II:

$$Cp^*—\overset{\overset{\textstyle Z'}{\diagdown}}{\underset{(X)_{n-1}}{\diagup}}M+ \qquad A^-$$

- 53 -
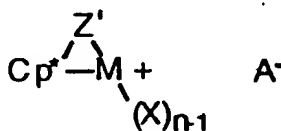
wherein:

Cp*, Z', M, X, and n are as defined with respect to previous formula I, and

5

A⁻ is a monovalent, noncoordinating, compatible anion, and

(c) contacting the product of (b) with a catalyst support comprising silica

reacted with a methylaluminoxane, a modified methylaluminoxane, or a mixture

thereof.

10

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F10/02   C08F4/643

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,92 05203 (EXXON CHEMICALS PATENTS INC.) 2 April 1992 see claims 1,2,4,5,7,14 & US,A,5 057 475 cited in the application	1-6,8, 14,15
Y	EP,A,0 418 044 (THE DOW CHEMICAL COMPANY) 20 March 1991 cited in the application see claims 1-17 see column 9, line 54 - line 57	1-6,8, 14,15

| | Further documents are listed in the continuation of box C. | [X] | Patent family members are listed in annex. |

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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